Studies of Halogenoacetato Cobalt(III) Complexes. II.[1],* The Preparation and Some Properties of *trans*-Bis(halogenoacetato)-tetrammine-cobalt(III) and *trans*-Bis(halogenoacetato)-bis(ethylenediamine)-cobalt(III) Complexes

By Kashiro KURODA and Philip S. GENTILE

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In the preceding communication,[1] the authors have reported on the *cis*-isomers of bis-(halogenoacetato)-tetrammine and bis(halogenoacetate)-bis(ethylenediamine) cobalt(III) complexes, *cis*-$[Co(halac)_2(NH_3)_4]^+$ and *cis*-$[Co(halac)_2(en)_2]^+$, where halac$=CH_3CO_2$, CH_2ClCO_2, $CHCl_2CO_2$, CCl_3CO_2, CH_2BrCO_2 and $CHBr_2CO_2$. There should be a geometrical isomer (trans-isomer) for each of the cis-isomers. Previously, Linhard and his co-workers[2,3] studied the complexes, $[Co(clac)_2(NH_3)_4]X$ and $[Co(clac)_2(en)_2]X$ (clac=acetato and three chloroacetato ligands); although they isolated many of the cis-isomers, only a few trans-isomers were obtained. The difficulties in the preparation of trans-isomers are to be attributed to the fact that the fraction of trans-isomer is small in a reaction product of a carbonato complex ($[CoCO_3(NH_3)_4]X$ or $[CoCO_3(en)_2]X$) and a halogenoacetic acid, and that no suitable reagent is known for the separation of geometrical isomers. As will be described in the following sections, the authors have found that trichloroacetic acid is an excellent precipitant for trans-isomers; it can separate them from mixtures which contain a large fraction of cis-isomers. As a result, many new species of the trans-isomers of bromoacetato-complexes as well as of chloroacetato-complexes have been isolated as trichloroacetates, and they have been converted to the perchlorates. Some of their physical and chemical properties have been studied, and interesting phenomena have been observed, especially in their absorption spectra.

Experimental

Materials.—Monochloroacetic, dichloroacetic and trichloroacetic acid (Fisher Scientific Co.), monobromoacetic acid (Eastman Organic Chemicals) and dibromoacetic acid (K & K Laboratories, Inc.), and all the other reagent-grade chemicals were used without further purification.

Analysis. — Cobalt was analyzed by a direct

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[*] The most part of this research was done in the laboratory of Department of Chemistry, Fordham University, New York 58, N. Y., U. S. A., during the period in which the former of the authors was a visiting chemist to the University.

[1] Part I of this series: K. Kuroda and P. S. Gentile, This Bulletin, **38**, 1362 (1965).

[2] M. Linhard and M. Weigel, *Z. anorg. Chem.*, **260**, 65 (1969); **264**, 321 (1951).

[3] M. Linhard and G. Stirn, ibid., **268**, 105 (1952).

TABLE I. ABSORPTION SPECTRA OF *trans*-[Co(halac)$_2$(NH$_3$)$_4$]ClO$_4$ AND *trans*-[Co(halac)$_2$(en)$_2$]ClO$_4$

	1st band				2nd band		3rd band	
	Ia		Ib					
	ν(10^{13}/sec.)	log ε	ν(10^{13}/sec.)	log ε	ν(10^{13}/sec.)	log ε	ν(10^{13}/sec.)	log ε
trans-[Co(halac)$_2$(NH$_3$)$_4$]ClO$_4$								
CH_3CO_2	54.5	1.806	shoulder		82.4	1.839	126	4.18
CH_2ClCO_2	54.0	1.818	shoulder		82.9	1.827	126	4.22
$CHCl_2CO_2$	53.8	1.795	shoulder		83.6	1.801	127*	4.20
CCl_3CO_2	53.3	1.798	65.7	1.38	84.0	1.778	128*	4.25
CH_2BrCO_2	54.1	1.835	shoulder		82.9	1.848	124.5	4.20
$CHBr_2CO_2$	53.9	1.846	shoulder		83.3	1.839	133.5*	4.26
trans-[Co(halac)$_2$(en)$_2$]ClO$_4$								
CH_3CO_2	55.8	1.778	66.7	1.462	84.0	1.863	128	4.25
CH_2ClCO_2	55.2	1.782	67.3	1.468	84.2	1.849	129	4.28
$CHCl_2CO_2$	54.8	1.771	67.9	1.471	84.5	1.831	—*	—
CCl_3CO_2	53.9	1.756	68.5	1.456	85.2	1.784	132*	4.33
CH_2BrCO_2	(not obtained in purity)							
$CHBr_2CO_2$	54.8	1.798	67.7	1.441	84.5	1.855	131*	4.33

Ionization constants of the halogenoacetic acids:

CH_3CO_2H	CH_2ClCO_2H	$CHCl_2CO_2H$	CCl_3CO_2H
1.75×10^{-5}	1.4×10^{-3}	5×10^{-2}	2×10^{-1}
	CH_2BrCO_2H	$CHBr_2CO_2H$	
	1.38×10^{-3}	?	

* Obvious deformation around max. is observed.

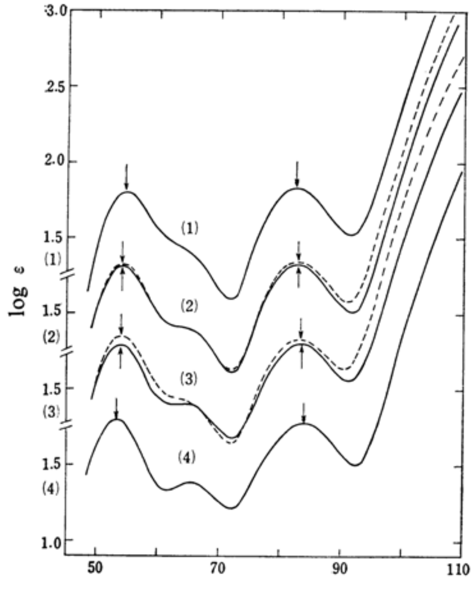

Fig. 1. Absorption spectra of *trans*-bis-(halogenoacetato)-tetrammine-cobalt(III) complexes.
(1) *trans*-[Co(CH$_3$CO$_2$)$_2$(NH$_3$)$_4$]ClO$_4$
(2) —— *trans*-[Co(CH$_2$ClCO$_2$)$_2$(NH$_3$)$_4$]ClO$_4$
- - - *trans*-[Co(CH$_2$BrCO$_2$)$_2$(NH$_3$)$_4$]ClO$_4$
(3) —— *trans*-[Co(CHCl$_2$CO$_2$)$_2$(NH$_3$)$_4$]ClO$_4$
- - - *trans*-[Co(CHBr$_2$CO$_2$)$_2$(NH$_3$)$_4$]ClO$_4$
(4) *trans*-[Co(CCl$_3$CO$_2$)$_2$(NH$_3$)$_4$]ClO$_4$

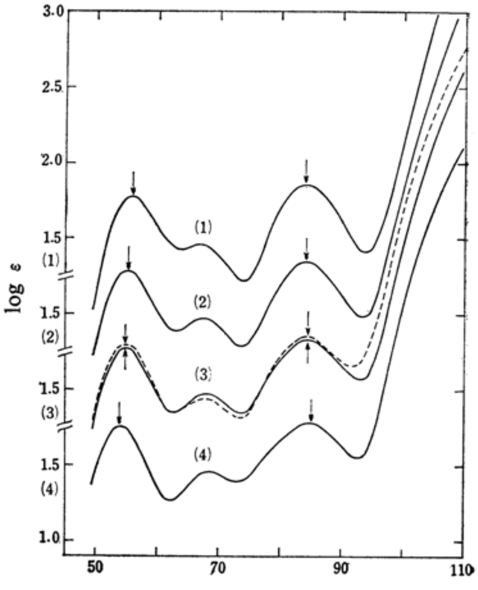

Fig. 2. Absorption spectra of *trans*-bis-(halogenoacetato)-bis(ethylenediamine)-cobalt-(III) complexes.
(1) *trans*-[Co(CH$_3$CO$_2$)$_2$(en)$_2$]ClO$_4$
(2) *trans*-[Co(CH$_2$ClCO$_2$)$_2$(en)$_2$]ClO$_4$
(3) —— *trans*-[Co(CHCl$_2$CO$_2$)$_2$(en)$_2$]ClO$_4$
- - - *trans*-[Co(CHBr$_2$CO$_2$)$_2$(en)$_2$]ClO$_4$
(4) *trans*-[Co(CCl$_3$CO$_2$)$_2$(en)$_2$]ClO$_4$

TABLE II. SOLUBILITIES AND PRECIPITATION REACTIONS OF THE PERCHLORATE OF *trans*-BIS(HALOGENOACETATO)-COBALT(III) COMPLEXES

Complex	HCl 6 N	NH_4Cl 2 N	HNO_3 6 N	NH_4NO_3 2 N	$HClO_4$ 6 N	$NaClO_4$ 2 N	NaBr 2 N	KI 2 N	$Na_2S_2O_3$ N	KSCN N	$K_2Cr_2O_7$ sat.	CCl_3CO_2H* 2 N	Solubility ml. H_2O/g.
trans-$[Co(CH_3CO_2)_2(NH_3)_4]^+$	4	—	—	—	3	—	—	1	—	—	—	2	17
trans-$[Co(CH_2ClCO_2)_2(NH_3)_4]^+$	—	—	—	—	2	2	—	1	—	—	—	4	108
trans-$[Co(CHCl_2CO_2)_2(NH_2)_4]^+$	—	—	—	—	2	2	—	1	—	—	2	4	20
trans-$[Co(CCl_3CO_2)_2(NH_3)_4]^+$	—	—	1	3	2	3	—	—	—	—	—	4	vs
trans-$[Co(CH_2BrCO_2)_2(NH_3)_4]^+$	—	—	—	—	2	3	—	1	—	—	—	4	77
trans-$[Co(CHBr_2CO_2)_2(NH_3)_4]^+$	—	—	—	—	3	3	1	4	—	1	3	4	54
trans-$[Co(CH_3CO_2)_2(en)_2]^+$	—	—	—	—	4	1	—	—	4	—	—	2	vs
trans-$[Co(CH_2ClCO_2)_2(en)_2]^+$	—	—	—	—	1	1	—	—	—	—	—	4	57
trans-$[Co(CHCl_2CO_2)_2(en)_2]^+$	—	—	—	—	1	2	—	—	—	—	—	4	260
trans-$[Co(CCl_3CO_2)_2(en)_2]^+$	—	—	—	—	4	4	—	3	—	2	—	4	370
trans-$[Co(CH_2BrCO_2)_2(en)_2]^+$	(not obtained in purity)												
trans-$[Co(CHBr_2CO_2)_2(en)_2]^+$	—	—	—	—	3	3	1	3	—	2	—	4	280

—: No precipitation
1: A small amount of deposit observable on the surface of the test tube
2: A small amount of precipitate
3: A large amount of precipitate (the liquid phase has still the color of the complex)
4: Almost complete precipitation (the liquid phase is almost colorless)
vs: Very soluble
* All cis-isomers of these complexes do not precipitate with trichloroacetic acid.

EDTA titration, using murexide as an indicator,[4] after the decomposition of a complex with hot concentrated sulfuric and nitric acid. The other elements were analyzed microquantitatively by the Schwarzkoph Microanalytical Laboratory (Woodside, New York, U. S. A.).

Apparatus and Measurments. — The absorption spectra of the complexes were measured with a Cary 15 spectrophotometer using a pair of 1 cm. quartz cells. The concentration of the complexes was 0.005 mol./1. (for *trans*-$[Co(CH_3CO_2)_2(en)_2]^+$, a 0.01 mol./1. solution was used) for the measurments in the visible and near ultraviolet region, whereas the original solutions were diluted to 0.0005 and 0.00005 mol./1. for the far ultraviolet region. In most cases, the complexes were dissolved in a 0.01 N and 0.04 N perchloric acid solution in order to avoid the possibility of a rapid base hydrolysis. It was found that a different concentration of the acid does not change the spectra. The spectra of the trichloroacetates of the complexes were also measured; it was found that the absorption curve was identical within the range of experimental error with that of the corresponding perchlorate in the visible and near ultraviolet region. The results are shown in Figs. 1 and 2 and Table I.

The solubility of the complexes was measured semiquantitatively in the same way as has been described in the previous report.[1] The precipitation reactions with various anions were also tested by a previously-reported[1] method. These experimental results are summarized in Table II.

Preparations. — *1) trans-Bis(acetato)-tetrammine-cobalt(III) Perchlorate, trans-*$[CO(CH_3CO_2)_2(NH_3)_4]ClO_4$*, and trans-Bis(monochloroacetato)-tetrammine-cobalt(III) Perchlorate, trans-*$[Co(CH_2ClCO_2)_2(NH_3)_4]ClO_4$. — These complexes were prepared by the method of Linhard and Weigel.[2]

2) trans-Bis(dichloroacetato)-tetrammine-cobalt(III) Perchlorate, trans-$[Co(CHCl_2CO_2)_2(NH_3)_4]ClO_4$. — A mixture of $[CoCO_3(NH_3)_4]ClO_4$ (5 g.), $CHCl_2CO_2H$ (10 g.) and water (10 ml.) was evaporated to almost complete dryness at 70—75°C. The cooled reaction product was mixed with 30 ml. of dilute perchloric acid and filtered with a glass-filter, then the residue on the filter was extracted with 10 ml. of alcohol. After the addition of 50 ml. of water to the extract, 3 g. of trichloroacetic acid was added and the solution was cooled to 0°C. The violet crystals formed were collected and washed with alcohol(10%)-ether mixture and ether. (If concentrated perchloric acid is added to the alcoholic extract, the perchlorate is obtained, but it is always contaminated with the cis-isomer, which is difficult to remove.) The yield of the trichloroacetate is ca. one gram. The trichloroacetate was dissolved in 60 ml. of a alcohol(90%)-water mixture and, after filtration, 20 ml. of concentrated perchloric acid was added. After the mixture had stood at 0°C, the resulting light violet crystals, the acidic salt, were collected on a filter and washed with ether in order to remove the aqueous phase mechanically as completely as possible, and then with absolute alcohol and ether. During the treatment with alcohol, the acidic salt changes to the neutral salt. Since the acidic salt is very soluble in alcohol when it is wet, it should be dry when it is treated with alcohol, as has been described above. Yield, 0.7 g.

Found: Co, 12.18; C, 10.06; H, 3.02; N, 11.80. Calcd. for *trans*-$[Co(CHCl_2CO_2)_2(NH_3)_4]ClO_4$: Co, 12.22; C, 9.96; H, 2.92; N, 11.62%.

3) trans-Bis(trichloroacetato)-tetrammine-cobalt(III) Perchlorate, trans-$[Co(CCl_3CO_2)_2(NH_3)_4]ClO_4$. — A solution of $[CoCO_3(NH_3)_4]ClO_4$ (3 g.) and CCl_3CO_2H (15 g.) in 10 ml. of water was evaporated to dryness at 70—75°C. The product was washed four times with 25 ml. portions of very dilute perchloric acid to remove the cis-isomer, and then extracted with 50 ml. of warm (~40°C) water. After three grams of CCl_3CO_2H had been added to the extract, the resulting light violet precipitate was collected and washed in the way described in 2). Yield of the trichloroacetate, 1.5 g. To convert it to the perchlorate, 1 g. of the trichloroacetate was dissolved in 30 ml. of water, and 15 ml. of a 50 per cent sodium perchlorate solution was added. The precipitate formed was washed as in 2). Yield, 0.6 g. Even if perchloric acid is used for the precipitation, the acidic perchlorate is obtained.

Found: Co, 10.43; C, 9.17; H, 2.46; N, 10.40. Calcd. for *trans*-$[Co(CCl_3CO_2)_2(NH_3)_4]ClO_4$: Co, 10.69; C, 8.71; H, 2.19; N, 10.16%.

4) trans-Bis(monobromoacetato)-tetrammine-cobalt(III) Perchlorate, trans-$[Co(CH_2BrCO_2)_2(NH_3)_4]ClO_4$. — A mixture of $[CoCO_3(NH_3)_4]ClO_4$ (5 g.), CH_2BrCO_2H (12.5 g.) and water (10 ml.) was evaporated to a small, tarry, volume at 60—65°C. The product was mixed with 20 ml. of a very dilute perchloric acid and the precipitate formed, after having been washed with a small amount of cold water, was extracted with 40 ml. of warm water. Two milliliters of concentrated perchloric acid was added to the extract, which was then cooled, and the violet precipitate formed was washed with a small amount of cold water, alcohol and ether. For further purification, the complex was converted once to the trichloroacetate and then to the perchlorate, as in 2). Yield, 0.7 g.

Found: Co, 11.66; C, 9.86; H, 3.32; N, 11.60. Calcd. for *trans*-$[Co(CH_2BrCO_2)_2(NH_3)_4]ClO_4$: Co, 11.73; C, 9.56; H, 3.21; N, 11.15%.

5) trans-Bis(dibromoacetato)-tetrammine-cobalt(III) Perchlorate, trans-$[Co(CHBr_2CO_2)_2(NH_3)_4]ClO_4$. — A mixture of $[CoCO_3(NH_3)_4]ClO_4$ (2 g.), $CHBr_2CO_2H$ (7 g.) and water (7 ml.) was evaporated at 70—75°C until crystals appeared. The product was mixed with 20 ml. of dilute perchloric acid, and the resulting precipitate was washed with 60 ml. of warm water. This treatment washed out the cis-isomer almost completely. (From the extract, the cis-isomer can be obtained by cooling.) The violet residue was dissolved in 100 ml. of warm water, and the solution was cooled to 0°C after the addition of several drops of perchloric acid. The violet crystals formed were washed with a small amount of cold water, an ethanol(10%)-ether mixture and ether. Yield, 0.7 g. The complex in the final filtrate is recoverable as the

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[4] H. Flaschka, *Mikrochemie ver. Mikrochim. Acta*, **39**, 38 (1952).

trichloroacetate by the addition of trichloroacetic acid. Yield of the trichloroacetate, 0.5 g.

Found: Co, 8.98; C, 7.40; H, 2.37; N, 8.60. Calcd. for *trans*-$[Co(CHBr_2CO_2)_2(NH_3)_4]ClO_4$: Co, 8.93; C, 7.28; H, 2.14; N, 8.49%.

6) trans-Bis(acetato)-bis(ethylenediamine)-cobalt(III) Perchlorate, trans-$[Co(CH_3CO_2)_2(en)_2]ClO_4$.—Although this compound had already been prepared by Linhard and Stirn,3) it was found that the following procedure was simpler and gave a high yield. A mixture of $[CoCO_3(en)_2]ClO_4$ (3 g.), CH_3CO_2H (4.5 g.) and water (5 ml.) was evaporated, using a small free flame, until solidification occurred. The product was mixed with 30 ml. of water, and, after filtration, 3 ml. of concentrated perchloric acid was added. The reddish crystals which formed were the acidic perchlorate, *trans*-$[Co(CH_3CO_2)_2(en)_2]ClO_4 \cdot HClO_4$; they were washed with dilute perchloric acid, ethanol and ether. Yield, 4.0 g. In order to obtain the neutral complex, 3 g. of the acidic salt was covered with ether in a flask, and anhydrous gaseous ammonia was bubbled through the mixture for ten minutes. The complex should be slightly wet; otherwise neutralization does not occur. The crystalline salt gained in volume by this treatment. After filtration, the residue on a filter was extracted with a small amount ($<$5 ml.) of warm ($\sim$40°C) water, and the filtrate was cooled sufficiently at 0°C. The red precipitate formed was washed with ethanol and ether. Yield, 0.5 g. After the dilution of the final filtrate to 50 ml. and the addition of perchloric acid, the complex can be recovered as the acidic perchlorate almost quantitatively.

Found: Co, 14.81; C, 24.32; H, 5.62; N, 14.20. Calcd. for *trans*-$[Co(CH_3CO_2)_2(en)_2]ClO_4$: Co, 14.86; C, 24.22; H, 5.59; N, 14.12%.

7) trans-Bis(monochloroacetato)-bis(ethylenediamine)-cobalt(III) Perchlorate, trans-$[Co(CH_2ClCO_2)_2(en)_2]ClO_4$. — A reaction product was obtained by the evaporation of a mixture of $[CoCO_3(en)_2]ClO_4$ (3 g.), CH_2ClCO_2H (7 g.) and water (10 ml.) at $\sim$70°C. It was mixed with 20 ml. of dilute perchloric acid, and the resulting precipitate was washed with ethanol and ether. The perchlorate thus obtained was dissolved in 180 ml. of warm water containing several drops of perchloric acid, and recrystallized. The violet crystals formed were washed with ethanol and ether. Yield, 2.0 g.

Found: Co, 12.63; C, 21.03; H, 4.56; N, 11.70. Calcd. for *trans*-$[Co(CH_2ClCO_2)_2(en)_2]ClO_4$: Co, 12.66; C, 20.64; H, 4.33; N, 12.03%.

8) trans-Bis(dichloroacetato)-bis(ethylenediamine)-cobalt(III) Perchlorate, trans-$[Co(CHCl_2CO_2)_2(en)_2]ClO_4$.—A product was obtained by the evaporation of a mixture of $[CoCO_3(en)_2]ClO_4$ (3 g.), $CHCl_2CO_2H$ (10 g.) and water at $\sim$70°C. The precipitate which was formed by the addition of dilute perchloric acid was extracted, with 100 ml. of warm water; then the extract was set aside. (This extract contains the cis-isomer.) A second separate extract was made with another 300 ml. of warm water; It was cooled after the addition of several drops of perchloric acid. The reddish purple crystals which formed were washed with cold dilute perchloric acid, ethanol and ether. Yield, 2.0 g.

Found: Co, 10.97; C, 18.14; H, 3.64; N, 10.40. Calcd. for *trans*-$[Co(CHCl_2CO_2)_2(en)_2]ClO_4$: Co, 11.03; C, 17.98; H, 3.40; N, 10.48%.

9) trans-Bis(trichloroacetato)-bis(ethylenediamine)-cobalt(III) Perchlorate, trans-$[Co(CCl_3CO_2)_2(en)_2]ClO_4$. — A mixture of $[CoCO_3(en)_2]ClO_4$ (2 g.), CCl_3CO_2H (8.5 g.) and water (6 ml.) was evaporated at $\sim$70°C to a small volume; then it was heated on a small flame until the color changed from dark red to deep violet. As soon as the color change was finished, the mixture was quickly cooled. The product was mixed with 20 ml. of dilute perchloric acid, and the resulting precipitate, after having been washed with a perchloric acid solution, was extracted with 100 ml. of an ethanol (50%)-water mixture. The last 80 ml. portion was separated from the first 20 ml., which was contaminated with the cis-isomer. After the addition of several drops of perchloric acid, the extract was cooled. The violet crystals which formed were washed in the way described in 2).

Found: Co, 9.54; C, 16.02; H, 2.86; N, 9.70. Calcd. for *trans*-$[Co(CCl_3CO_2)_2(en)_2]ClO_4$: Co, 9.77; C, 15.92; H, 2.67; N, 9.29%.

10) trans-Bis(monobromoacetato)-bis(ethylenediamine)-cobalt(III) Perchlorate, trans-$[Co(CH_2BrCO_2)_2(en)_2]ClO_4$.—This complex was not isolated in a highly pure state. Many procedures similar to those used for the others were tried, but the reaction products were always very hygroscopic, as in the case of *cis*-$[Co(CH_2BrCO_2)_2(en)_2]ClO_4$. Trichloroacetic acid could form a precipitate with some of the reaction products, and although the spectra showed a fairly satisfactory feature (a large splitting of the first band), it was also hygroscopic.

11) trans-Bis(dibromoacetato)-bis(ethylenediamine)-cobalt(III) Perchlorate, trans-$[Co(CHBr_2CO_2)_2(en)_2]ClO_4$. — A mixture of $[CoCO_3(en)_2]ClO_4$ (2 g.), $CHBr_2CO_2H$ (7 g.) and water (5 ml.) was evaporated at 65—70°C and then heated and boiled carefully on a small flame for a few minutes. When the color suddenly changed from dark red to reddish-violet, the mixture was quickly cooled. The precipitate, which was formed by the addition of dilute perchloric acid, was washed with a dilute perchloric acid and then extracted with 150 ml. of an ethanol(75%)-water mixture. The last 120 ml. protion, which was kept separate from the first 30 ml., was cooled after the addition of several drops of perchloric acid. The dark purple crystals which formed were washed with ethanol and ether. Yield, 1.5 g.

Found: Co, 8.22; C, 13.78; H, 2.77; N, 7.94. Calcd. for *trans*-$[Co(CHBr_2CO_2(en))_2]ClO_4$: Co, 8.27; C, 13.49; H, 2.55; N, 7.87%.

Discussion

Preparation. — Linhard and his co-workers2) studied the $[Co(clac)_2(NH_3)_4]X$ complexes and found that the cis-isomer was obtained when an aqueous solution of $[CoCO_3(NH_3)_4]ClO_4$ and an equivalent amount of a chloroacetic acid was evaporated at a relatively low temperature, whereas the *trans*-isomer was obtained when a large excess of chloroacetic acid was used and the evaporation occurred at a higher temperature. With dichloroacetato- and trichloroacetato-complexes, however, they could not isolate the trans-isomers.

The same principle was applied in the preparation of all the complexes which were studied in this report, (the preparations of cis-isomers have been reported already) ;[1] it was observed again that it was easier to isolate cis-isomers than trans-isomers, except for acetato-complexes. It was also noted that the yield of trans-isomers was small, especially for ligands with a high halogen content. Therefore, along with the known procedures, two new techniques were applied whereby the trans-isomer can be separated from a large amount of cis-isomer and/or the yield of trans-isomer can be raised. First, as has been described in the Experimental section and as may be seen in Table II, it was found that trichloroacetic acid selectively precipitated trans-isomers and that, therefore, a small quantity of trans-isomer could be isolated from a mixture containing a large quantity of cis-isomer. This method was applied in the isolation of *trans*-$[Co(CHCl_2CO_2)_2(NH_3)_4]^+$ and *trans*-$[Co(CCl_3CO_2)_2(NH_3)_4]^+$, and in the purification of the others.

Second, after the evaporation of the solution of the starting materials had nearly been completed, the product was boiled for a short time. In the bis(ethylenediamine)- series, the coordination of ethylenediamine is still stable at a high temperature; therefore, boiling the reaction mixture causes a rapid rearrangement of the cis- to the trans-configuration, resulting in a higher yield of the trans-isomer. This technique was used for the preparation of *trans*-$[Co(CCl_3CO_2)_2(en)_2]ClO_4$ and *trans*-$[Co(CHBr_2CO_2)_2(en)_2]ClO_4$. In the tetrammine-series, however, there is a possibility of the decomposition of the complexes themselves.

Solubilities and Precipitation Reactions.— Similarly to the case of cis-isomers,[1] it was noted that complexes with a large halogen content are soluble in alcohol or even in an alcohol-ether mixture, especially when they are slightly moist. One should therefore be careful in the washing of the complexes in their preparations.

In addition to the anions listed in Table II, it was observed that 1 N solution of sodium carbonate, sodium nitrite, sodium acetate, potasium chromate, sodium sulfite or sodium oxalate, and a saturated solution of sodium hydrogen phosphate, 6 N sulfuric acid and 2 N ammonium sulfate did not precipitate with any of the complexes. As has been described in the Experimental section, most of the *trans*-isomers form acidic salts with perchloric acid. In the cases of two acetato-complexes, acidic salts are relatively insoluble compared with the neutral salts; therefore, precipitation occurs upon the addition of perchloric acid but not upon that of sodium perchlorate. Similar phenomena take place in *trans*-$[Co(CH_3CO_2)_2(NH_3)_4]^+$ with hydrogen chloride and ammonium chloride.

Absorption Spectra.—The visible and ultraviolet absorption spectra of the *trans*-$[Coa_4b_2]$ complexes are of especial interest because of a large splitting which occurs in the first band. All of the present complexes showed the splitting, as can be seen in Figs. 1 and 2, by which the assignment of the geometrical configuration has been made.

Shimura[5] proposed an empirical rule regarding the relative positions between the maxima of cis- and trans-isomers of Coa_4b_2:

$$\nu_{\mathrm{cis}}-\nu_{\mathrm{trans}} \lesseqqgtr 0$$

$$\text{if "a" is to the}\left\{\begin{array}{l}\text{left (I side)}\\ \text{identical}\\ \text{right (CN side)}\end{array}\right\}\text{of "b" in}$$

the spectrochemical series; this rule has been supported theoretically.[6] Concerning the present complexes, NH_3 or en (a) is to the right of the halogenoacetato ligands (b), and the ν_{cis}'s are larger than the corresponding ν_{trans}'s thereby confirming Shimura's rule.

The order of the ligands in the spectrochemical series has already been determined to be :[1]

$$\mathrm{I}<\cdots<\mathrm{CH_3CO_2}<$$
$$\left\{\begin{array}{l}\mathrm{CH_2ClCO_2}<\mathrm{CHCl_2CO_2}<\mathrm{CCl_3CO_2}\\ \qquad\wr\qquad\qquad\quad\wr\\ \mathrm{CH_2BrCO_2}<\mathrm{CHBr_2CO_2}(<\mathrm{CBr_3CO_2})\end{array}\right\}<$$
$$\cdots<\mathrm{NH_3}<\mathrm{en}<\cdots<\mathrm{CN}$$

(increasing ligand field)

and it has been verified that the basicity of the ligands is the main factor in determining the spectral characteristic of each series of halogenoacetato-complexes. Therefore, it may be said that the degree of splitting increases with an increase in the halogen content in the halogenoacetato-ligands, or with a decrease in the basicity of the ligands, as may be seen in Table I and the figures.

Since the spectrochemical series represents the order of the strengths of the ligand fields, the tetragonality (tetragonal deviation from a cubic symmetry) of a Coa_4b_2 complex increases with the increase in the distance between "a" and "b" in the series. According to the ligand field theory, the

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[6] L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

[7] C. J. Ballhausen and C. K. Jörgensen, *Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd.*, **29**, (14) (1955).

magnitude of the band splitting depends on the degree of tetragonality.[7] Therefore, it may be predicted that the splitting in the acetato-complex will be the largest and that in the trichloroacetato-complex the smallest. However, this predicted order seems to be entirely the reverse of the observed order. This reversal is considered to be of interest; further examination of the spectral curves is needed for an interpretation. After an analysis of the curves separating into single bands, a quantitative consideration of the band splitting will be reported.

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Department of Chemistry
Kyoto Gakugei University
Fushimi-ku, Kyoto(K.K.)

Department of Chemistry
Fordham University
New York 58, N. Y. (P. S. G.)